

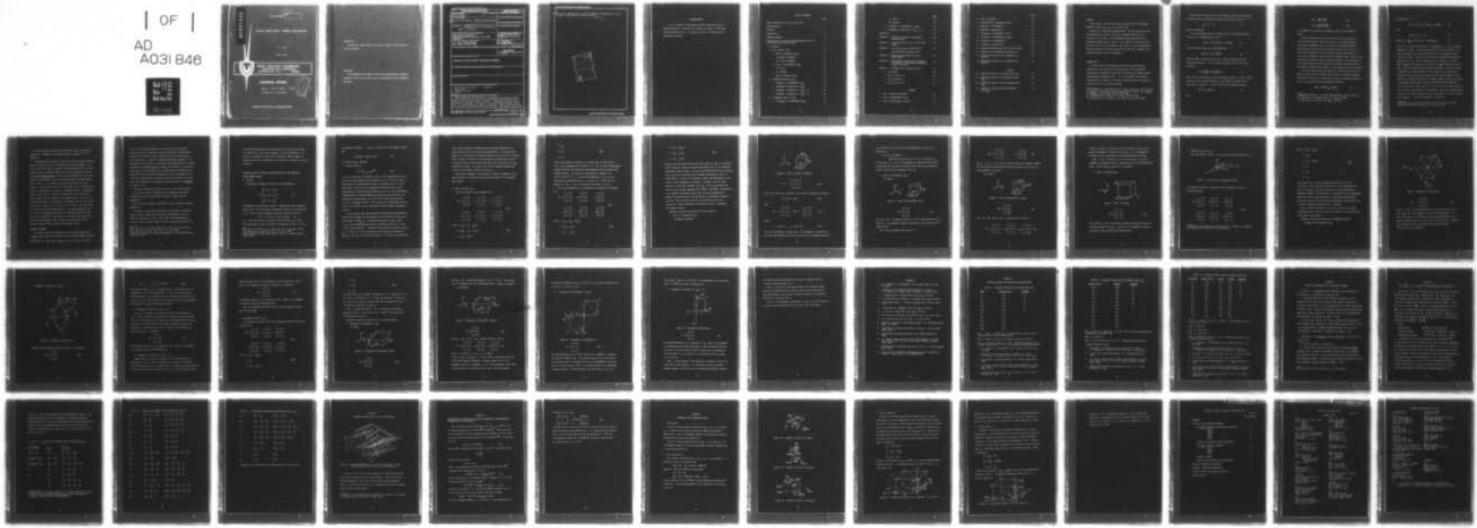
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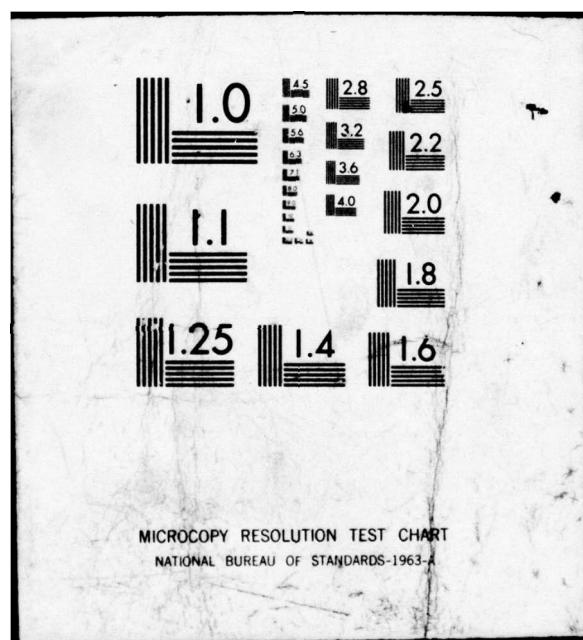
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CRYSTALS UNDER STRAIN: SYMMETRY CONSIDERATIONS

D. M. Gray

October 1976



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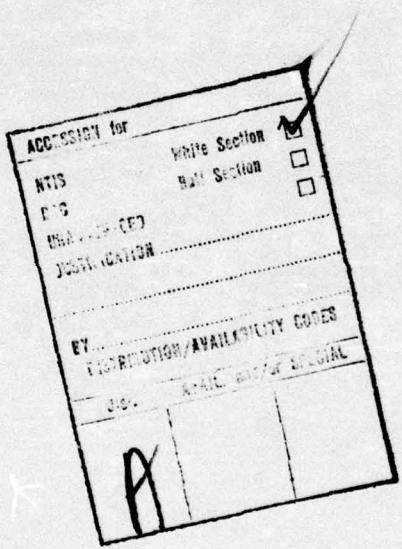
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exist due to symmetry alone. Specific examples for deformations of cubic, hexagonal, and tetragonal crystals are given.



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## TABLE OF CONTENTS

	<b>Page</b>
Report Documentation Page, DD Form 1473	
Acknowledgement	i
Notation	1
Introduction	1
Symmetry Theorems	5
Decomposition of the Strain and Determination of the Associated Lower Symmetry Groups	7
A. General	7
B. Cubic Crystals ( $O_h$ )	9
1. Cubic $\rightarrow$ Tetragonal ( $D_{4h}$ )	11
(a) General Tetragonal	11
(b) " $\Gamma_{12}$ " Tetragonal	13
2. Cubic $\rightarrow$ Orthorhombic ( $D_{2h}$ )	13
(a) "Even"	13
(b) "Uneven"	14
3. Cubic $\rightarrow$ Trigonal ( $D_{3d}$ )	15
C. Hexagonal Crystals ( $D_{6h}$ )	16
1. Hexagonal $\rightarrow$ Orthorhombic ( $D_{2h}$ )	17
2. Hexagonal $\rightarrow$ Monoclinic P ( $C_{2h}$ )	19
3. Hexagonal $\rightarrow$ Monoclinic C ( $C_{2h}$ ) - xz	20
4. Hexagonal $\rightarrow$ Monoclinic C ( $C_{2h}$ ) - yz	20
D. Tetragonal Crystals ( $D_{4h}$ )	21
1. Tetragonal $\rightarrow$ Orthorhombic ( $D_{2h}$ )	22

	Page
(a) "Even"	22
(b) "Uneven"	23
2. Tetragonal $\rightarrow$ Orthorhombic C ( $D_{2h}$ )	24
3. Tetragonal $\rightarrow$ Monoclinic P ( $C_{2h}$ ) - xz	25
References	27
Appendix A. Equivalent Labels for Irreducible Representations	28
Appendix B. Proof of Corollaries to the Star-of- $\bar{k}$ Theorem	31
Appendix C. Use of $[\Gamma_{xyz}]_s$ to Generate the Representations Contained in $\bar{e}$	32
Appendix D. Subgroup Decomposition of the 32 Point Groups	36
Appendix E. Transformation Properties of Operators Determined by Transformation Properties of Basis Functions	37
Appendix F. Hexagonal Case: Geometric Details	39
1. $\Gamma_1$ Strains	39
2. The $\Gamma_6$ Strain xy	39
3. The $\Gamma_5$ Strain xz	41
4. The $\Gamma_5$ Strain yz	42

### FIGURES

1. Cubic $\rightarrow$ General Tetragonal	12
2. Cubic $\rightarrow$ Orthorhombic "Even"	13
3. Cubic $\rightarrow$ Orthorhombic "Uneven"	14

	Page
4. Cubic → Trigonal	15
5. Coordinates for Hexagonal Crystals	16
6. Hexagonal → Orthorhombic	18
7. Hexagonal → Monoclinic P	19
8. Tetragonal → Orthorhombic "Even"	22
9. Tetragonal → Orthorhombic "Uneven"	23
10. Tetragonal → Orthorhombic C	24
11. Tetragonal → Monoclinic P	25
12. Subgroup Decomposition of the 32 Point Groups	36
13. Geometry for the Hexagonal $\Gamma_6$ Strain xy	40
14. Perspective Drawing for the Hexagonal $\Gamma_5$ Strain xz	41
15. Perspective Drawing for the Hexagonal $\Gamma_5$ Strain yz	42

#### TABLES

A-1. Equivalent Labels for the Cubic Group ( $O_h$ )	28
A-2. Equivalent Labels for the Hexagonal Group ( $D_{6h}$ )	29
A-3. Equivalent Labels for the Tetragonal Group ( $D_{4h}$ )	30
C-1. Irreducible Representations Contained in $[\Gamma_{xyz}]_s$	33

## NOTATION

Point groups: For the point groups (crystal class) the standard Schönflies labels ( $O_h$ ,  $C_{2h}$ ,  $D_3$ , etc.) are used.

Labeling of irreducible representations: For the cubic group ( $O_h$ ) the BSW notation<sup>1</sup> is used.  $\Gamma_i$  for the tetragonal group ( $D_{4h}$ ) is identical to  $X_i$  of BSW. For the hexagonal group ( $D_{6h}$ ) and for the additional groups listed in Table C-1 the notation is essentially that of Koster et al.<sup>2</sup>; we have replaced  $\Gamma_i+$  with  $\Gamma_i$ . The correspondence between frequently used labeling systems for the cubic, hexagonal, and tetragonal groups is shown in Appendix A.

## INTRODUCTION

A useful check on the crystal potential used in an electronic bandstructure calculation may be obtained from a first-principles determination of deformation potentials if these can be checked against experimentally determined values. It is well known<sup>3,4</sup> that strains associated with a change in the crystal symmetry provide a particularly critical test of the original potential.

<sup>1</sup>L.P. Bouckaert, R. Smoluchowski, and E. Wigner, Phys. Rev. 50, 58 (1936)

<sup>2</sup>"Properties of the Thirty-Two Point Groups", G.F. Koster, J.O. Dimmock, R.G. Wheeler, and H. Statz (M.I.T. Press, 1963).

<sup>3</sup>D. Shoenberg and B.R. Watts, Philos. Mag. 15, 1275 (1967).

<sup>4</sup>R. Griessen and R.S. Sorbello, J. Low Temp. Phys. 16, 237 (1974).

The motivation behind the use of perturbation theory is very simple; one wants to avoid calculating the small energy shifts  $\Delta E$  from a

$$\Delta E = E^1 - E^0 \quad (1)$$

type of calculation.

In the unperturbed crystal the energy levels are determined from a solution of the Schrödinger equation,

$$[-\nabla^2 + V(\vec{r})] \psi^0(\vec{r}) = E^0 \psi^0(\vec{r}). \quad (2)$$

The electron wave function is approximated by

$$\psi_n^0(\vec{r}) = \sum_i c_i^n \phi_i^0(\vec{r}) \quad (3)$$

where the  $\phi_i^0$  are known functions and the  $c_i^n$  are determined by the variational procedure. The variational procedure leads to the set of equations

$$\sum_j c_j^n \langle \phi_i^0 | H^0 - E_n^0 | \phi_j^0 \rangle = 0 \quad (4)$$

where  $H^0$  is the Hamiltonian of the unperturbed system  $H_0 = (-\nabla^2 + V^0(\vec{r}))$  and  $E_n^0$  is the  $n$ th energy eigenvalue. (We arbitrarily order the  $E^0$ 's from lowest to highest.) In matrix form the last equation becomes

$$\overline{H}^0 \vec{c}_n = E_n^0 \overline{S}^0 \vec{c}_n, \quad (5)$$

with

$$S^0_{ij} = \langle \phi_i^0 | \phi_j^0 \rangle \quad (6a)$$

$$H^0_{ij} = \langle \phi_i^0 | H^0 | \phi_j^0 \rangle \quad (6b)$$

As the  $\phi_i^0$  are not necessarily orthogonal,  $\bar{S}^0$  is not the identity matrix.

From the computational point of view there are two reasons for utilizing Group Theory in the  $E^0$  problem: (1) to provide automatic accounting of degeneracy and of the connectivity between different-magnitude  $\vec{k}$  points along the same symmetry direction in  $\vec{k}$  space. (2) To decrease the number of trial expansion functions  $\phi_i$  necessary to obtain good convergence (and thus decrease computer time). Both of these stem from a general principle of quantum mechanics; the wave functions of a quantum system must form bases for irreducible representations of the group of operators which commute with the Hamiltonian of the system.<sup>5</sup>

In the modified-plane-wave formulation<sup>6,7</sup> within which we work the  $\phi$ 's are plane waves and atomic-like functions. The plane wave  $\phi$ 's change under strain due to containing the lattice constant(s) explicitly. Thus, the usual first-order perturbation expression

$$\Delta E_n = \langle \psi_n^0 | H_{\text{pert}} | \psi_n^0 \rangle \quad (7)$$

<sup>5</sup>"Energy Band Theory", J. Callaway (Academic Press, 1964), Section 1.6.

<sup>6</sup>E. Brown and J.A. Krumhansl, Phys. Rev. 109, 30 (1958).

<sup>7</sup>D. Gray and E. Brown, Phys. Rev. 160, 567 (1967).

is replaced by

$$\Delta E_n = \sum_{ij} c_i^n c_j^n (\Delta H_{ij} - E_n^0 \Delta S_{ij}) \quad (8)$$

with

$$\Delta H_{ij} \equiv H_{ij}^1 - H_{ij}^0 \quad (9)$$

$$\text{where } H_{ij}^1 = \langle \phi_i | -\nabla^2 + V^0(r) + \Delta V(r) | \phi_j \rangle. \quad (10)$$

(See ref 8; in particular Section II and Appendix A.)  $\Delta S_{ij}$  is defined analogously to  $\Delta H_{ij}$ . Three important points should be noted here: (1)  $\Delta H_{ij}$  (and  $\Delta S_{ij}$ ) are obtained algebraically by expanding  $H_{ij}^1$  ( $S_{ij}^1$ ) in a Taylor series. (Otherwise, one has merely shifted the subtraction approach of eq (1) to the individual  $S_{ij}$ ,  $H_{ij}$  elements.) (2) Both  $H_{ij}^1$ ,  $S_{ij}^1$  and  $H_{ij}^0$ ,  $S_{ij}^0$  must be expressed in the lower symmetry for those cases in which the perturbation changes the symmetry. (Once the crystal is deformed, the higher symmetry of the original crystal has no real meaning, thus  $H_{ij}^1$ ,  $S_{ij}^1$  must be expressed in the lower symmetry; if one then tries to express  $H_{ij}^0$ ,  $S_{ij}^0$  in the higher symmetry, there is no simple correspondence between the  $ij$  labels of  $\bar{H}^0$ ,  $\bar{S}^0$  and those of  $\bar{H}^1$ ,  $\bar{S}^1$ .) (3) To first order  $\Delta V(r)$  equals zero if both of the following conditions hold: (A) The strain contains no  $\Gamma_1$  component (that strain component which preserves the original symmetry); (B)  $V(r)$  and  $\Delta V(r)$  are taken as spherically symmetric. (See ref 9, Appendix A, section A.)

8A.M. Gray, D.M. Gray, and E. Brown, Phys. Rev. B, 11, 1475 (1975).

9D.M. Gray and A.M. Gray, Phys. Rev. B, 14, 669 (1976).

For cubic crystals, explicit expressions for  $\Delta S_{ij}$  and  $\Delta H_{ij}$  for hydrostatic, tetragonal, and trigonal strains are given in ref 8, Appendix C.

In applying this procedure to specific crystal and strain types one needs to know what group is associated with the lower symmetry. The main part of this report is devoted to the determination of this lower symmetry group for various strains and to what simplifying relations exist due to symmetry alone. Once the group associated with the lower symmetry is identified, extensive use may be made of existing compatibility tables. As an example, consider a  $\Gamma_{25}'$  level of a cubic crystal. In the unperturbed ( $E^0$ ) case  $\Gamma_{25}'$  levels are 3-fold degenerate ( $\Gamma_{25}'$  is 3-dimensional). Now apply a tetragonal strain. Compatibility tables (connecting the tetragonal subgroup to the full cubic group) associate  $\Gamma_{25}'$  with  $\Gamma_3$  and  $\Gamma_5$  of the tetragonal group. Since  $\Gamma_3$  is 1-dimensional and  $\Gamma_5$  is 2-dimensional, one immediately knows that, under this strain, a  $\Gamma_{25}'$  level will split into two levels, one non-degenerate ( $\Gamma_3$ ) and one 2-fold degenerate ( $\Gamma_5$ ). The unperturbed  $\Gamma_{25}'$  level will show up on  $\Gamma_3$  and on  $\Gamma_5$  whereas the different shifts will show up only on  $\Gamma_3$  or  $\Gamma_5$ , as appropriate; in this particular example one need only compute one of these two shifts, the other may then be deduced immediately from symmetry considerations alone.

#### SYMMETRY THEOREMS

The example just given illustrates a major simplification due to symmetry; this simplification stems from the following theorem (proved

<sup>8</sup>A.M. Gray, D.M. Gray, and E. Brown, Phys. Rev. B, 11, 1475 (1975).

in ref 9): The Fermi energy  $E_F$  and the sum over the "star-of- $\vec{k}$ " of any given level belonging to any given irreducible representation changes (to first-order) under strain only if the strain contains a  $\Gamma_1$  component (i.e., contains a symmetry-preserving component). This theorem allows one to make, from symmetry considerations alone, a number of predictions regarding ratios of energy level shifts<sup>8</sup>. It should be noted that no more information can be obtained from the Wigner-Eckart theorem<sup>8,10</sup> than from standard compatibility tables combined with the "star-of- $\vec{k}$ " theorem above; the Wigner-Eckart theorem leads to the same ratios and corroborates the information that some shifts are probably not equal to zero.

There are two important corollaries to the "star-of- $\vec{k}$ " theorem:

- (1) For cubic crystals,  $\Delta\text{Volume}=0$  is the necessary (except for "accidental" cases) and sufficient condition for  $\Delta E_F$  (etc.)=0. (Appendix B).
- (2) For non-cubic crystals,  $\Delta\text{Volume}=0$  is only a necessary condition. (Appendix B).

If a model is chosen which constrains the potential to spherical symmetry within a muffin-tin sphere (after deformation as well as before) the discussion in ref 9 shows that our theorem applies to  $V(r)$  also; thus, for such a model, and for strains not containing  $\Gamma_1$ ,

<sup>8</sup>A.M. Gray, D.M. Gray, and E. Brown, Phys. Rev. B, 11, 1475 (1975).

<sup>9</sup>D.M. Gray and A.M. Gray, Phys. Rev. B, 14, 669 (1976).

<sup>10</sup>"Operator Techniques in Atomic Spectroscopy," B.R. Judd (McGraw-Hill, 1963), pp. 39-41.

the bandstructure shifts and splittings are due solely to the change in symmetry and to the explicit change in lattice constant(s), i.e., there is a "geometric" effect but no "potential" effect (change in bandstructure due to the change in  $V(r)$  caused by the change in lattice constant).

#### DECOMPOSITION OF THE STRAIN AND DETERMINATION OF THE ASSOCIATED LOWER SYMMETRY GROUPS

##### A. General.

An arbitrary (symmetric) strain can be represented as

$$\bar{e} = \begin{bmatrix} e_{11} & e_{12} & e_{13} \\ e_{12} & e_{22} & e_{23} \\ e_{13} & e_{23} & e_{33} \end{bmatrix} \quad (11)$$

The components are defined as follows: imagine that three orthogonal axes  $\hat{f}_0$ ,  $\hat{g}_0$ ,  $\hat{h}_0$  of unit length are imbedded securely in the unstrained solid. After a small deformation these axes become  $\hat{f}$ ,  $\hat{g}$ ,  $\hat{h}$  with

$$\hat{f} = (1 + e_{11}) \hat{f}_0 + e_{12} \hat{g}_0 + e_{13} \hat{h}_0 \quad (12)$$

etc. (This definition is consistent with that used in ref 8 and 9 and corresponds to Kittel's notation<sup>11</sup> except for a factor 1/2 in the

<sup>8</sup>A.M. Gray, D.M. Gray, and E. Brown, Phys. Rev. B, 11, 1475 (1975).

<sup>9</sup>D.M. Gray and A.M. Gray, Phys. Rev. B, 14, 669 (1976).

<sup>11</sup>"Introduction to Solid State Physics", 2nd ed., C. Kittel (Wiley, 1956), Chap. 4.

off-diagonal elements.) From eq (11) and (12) it may readily be seen that

$$\Delta \text{Volume} = (\text{Volume}) \text{ Tr } \bar{\bar{e}} \quad (13)$$

by writing  $\text{Volume} = \vec{f} \times \vec{g} \cdot \vec{h}$ .

We may write  $\bar{\bar{e}}$  as

$$\bar{\bar{e}} = \sum_{i,\alpha} c_{i\alpha} \bar{e}^{i\alpha} \quad (14)$$

i.e., as a linear sum of component strains, each transforming like one partner of one irreducible representation. (In eq (14) the  $i$  index is associated with a representation label; the  $\alpha$  index allows for cases where there is more than one independent  $\bar{e}$  associated with a given representation, either through different partners of a multi-dimensional representation or through independent functions associated with a one-dimensional representation, e.g.,  $x^2+y^2$  and  $z^2$  both associated with  $\Gamma_1$  for a tetragonal crystal.) Since there are six independent entities in eq (11) six  $\bar{e}^{i\alpha}$  will be required for the most general (symmetric) strain  $\bar{\bar{e}}$ .

For any crystal class (point group) the irreducible representations which may be included in the decomposition of an arbitrary strain must be contained in  $[\Gamma_{xyz}]_s$ , the symmetrized square of  $\Gamma_{xyz}$ , where  $\Gamma_{xyz}$  is the representation (possibly reducible) which has  $x$ ,  $y$ , and  $z$  as its basis functions. (A proof of this theorem is outlined in Appendix C; Table C-1 lists the irreducible representations contained in  $[\Gamma_{xyz}]_s$  for all of the 32 point groups.) This does not automatically

tell us which strains are associated with which representations but does restrict the list of possible representations. For a given point group this list may also be obtained indirectly if the list for a "parent" group is known; for example, the tetragonal point group ( $D_{4h}$ ) list may be obtained from the cubic point group ( $O_h$ ) list by using the  $O_h \leftrightarrow D_{4h}$  compatibility tables. An overall chart of the subgroup decomposition of the 32 point groups is shown in Appendix D.

Using cubic, hexagonal, and tetragonal crystals as examples, we now show how specific strains are associated with specific lower-symmetry point groups.

### B. Cubic Crystals ( $O_h$ ).

For cubic crystals we may decompose  $\mathbf{e}$  as

$$\begin{aligned} \tilde{\mathbf{e}} = & a \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} + b \begin{bmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 2 \end{bmatrix} + c \begin{bmatrix} 1 & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 0 \end{bmatrix} \\ & + d \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix} + f \begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix} + h \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \end{aligned} \quad (15a)$$

$$\text{with } a = (e_{11} + e_{22} + e_{33})/3$$

$$b = (2e_{33} - e_{11} - e_{22})/6 \quad (15b)$$

$$c = (e_{11} - e_{22})/2$$

$$d = e_{23}$$

$$f = e_{13}$$

(15b)

$$h = e_{12}$$

Using the procedure of Appendix E, one finds that the first matrix in eq (15a) transforms like  $x^2+y^2+z^2$ , i.e., like  $\Gamma_1$  (the correspondence between functions and irreducible representations can be obtained from standard tables); the second and third matrices transform like  $2z^2-x^2-y^2$  and  $x^2-y^2$ , i.e., like the two partners of  $\Gamma_{12}$ ; the last three matrices transform like  $yz$ ,  $xz$ , and  $xy$ , i.e., like the three partners of  $\Gamma_{25}$ . This is consistent with Table C-1 for  $O_h$ .

For actual computation it is probably more convenient to decompose

$\bar{e}$  as

$$\bar{e} = a \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} + b \begin{bmatrix} 1 & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 2 \end{bmatrix} + c \begin{bmatrix} 2 & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & \bar{1} \end{bmatrix} \quad (16a)$$

$$+ d \begin{bmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{bmatrix} + f \begin{bmatrix} 0 & \bar{1} & \bar{1} \\ \bar{1} & 0 & 1 \\ \bar{1} & 1 & 0 \end{bmatrix} + h \begin{bmatrix} 0 & 1 & \bar{1} \\ 1 & 0 & \bar{1} \\ \bar{1} & \bar{1} & 0 \end{bmatrix}$$

$$\text{with } a = (e_{11} + e_{22} + e_{33})/3$$

$$b = (e_{33} - e_{22})/3$$

(16b)

$$c = (e_{11} - e_{22})/3$$

$$d = (e_{12} + e_{23})/2$$

$$f = (e_{23} - e_{13})/2 \quad (16b)$$

$$h = (e_{12} - e_{13})/2$$

Using eq (13) one sees that only the first matrix in (16a) is associated with a change in volume; this matrix transforms like  $\Gamma_1$  and represents hydrostatic (cubic) strain. The second and third matrices each transform like  $\Gamma_{12}$  and are associated with tetragonal distortions; since the third matrix is related to the second by simply interchanging the x and z axes, no new computation is required. Similarly, the last three matrices in (16a) each transform like  $\Gamma_{25}$  and are associated with strains along the long diagonals  $\langle 111 \rangle$ ,  $\langle \bar{1}11 \rangle$ , and  $\langle \bar{1}\bar{1}1 \rangle$ , respectively, i.e., trigonal distortions; again, only one actual computation is needed, the remaining two being determined by interchange of appropriate axes. Thus, for cubic crystals, an arbitrary strain may be written as a linear combination of hydrostatic (cubic), tetragonal, and trigonal strains.

Examples of specific distortions of cubic crystals:

1. Cubic  $\rightarrow$  tetragonal ( $D_{4h}$ ).

(a) General tetragonal.

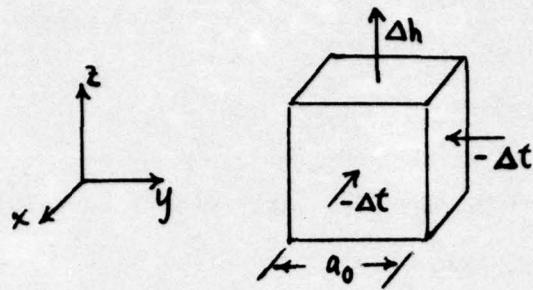


Figure 1. Cubic  $\rightarrow$  general tetragonal.

$$\bar{\bar{e}} = e \begin{bmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & \alpha \end{bmatrix} \quad (17a)$$

with  $e a_0 = \Delta t$  and  $\alpha = \Delta h / \Delta t$ . This is most conveniently written as

$$\bar{\bar{e}} = c_1 \bar{\bar{e}}^1 + c_2 \bar{\bar{e}}^2 \quad (17b)$$

with

$$\bar{\bar{e}}^1 = e \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \quad \bar{\bar{e}}^2 = e \begin{bmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 2 \end{bmatrix} \quad (17c)$$

giving

$$c_1 = (\alpha - 2)/3, \quad c_2 = (\alpha + 1)/3. \quad (17d)$$

Thus, for an arbitrary  $\Delta h / \Delta t$  ratio a  $\Gamma_1$  component is required and the star-of- $\bar{k}$  theorem does not hold; there are two "operator functions",

$c_1 (x^2+y^2+z^2)$  and  $c_2 (2z^2-x^2-y^2)$  transforming like  $\Gamma_1$  and  $\Gamma_{12}$ , respectively.

(b) " $\Gamma_{12}$ " tetragonal.

When  $\Delta h$  is exactly  $2\Delta t$  (i.e.,  $\alpha = 2$ ) we see from eq (17d) that  $c_1 = 0$  and no  $\Gamma_1$  component is required so that volume is preserved and the star-of- $\vec{k}$  theorem holds; the operator function is then  $2z^2-x^2-y^2$  which transforms like  $\Gamma_{12}$ .

2. Cubic  $\rightarrow$  orthorhombic ( $D_{2h}$ ).

(a) "Even".

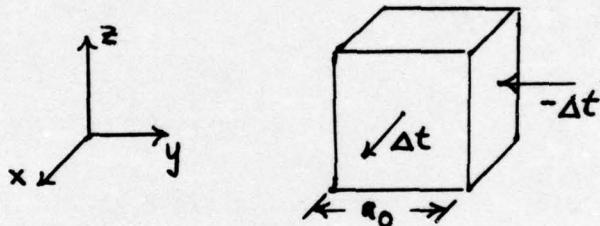


Figure 2. Cubic  $\rightarrow$  orthorhombic "even".

$$\bar{\epsilon} = e \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (18)$$

with  $e a_0 = \Delta t$ . The operator function is  $x^2-y^2$ , second partner of  $\Gamma_{12}$ . There is no  $\Gamma_1$  component (volume is preserved); thus, the star-of- $\vec{k}$  theorem holds.

Note: We may represent this strain as

$$\bar{\bar{e}} = c_1 e \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 2 \end{bmatrix} + c_2 e \begin{bmatrix} 2 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (19)$$

with  $c_1 = 1/3$ ,  $c_2 = 2/3$  so that, if one already has a computer program for the distortion associated with the first matrix of eq (19), no new programming is required.

(b) "Uneven".

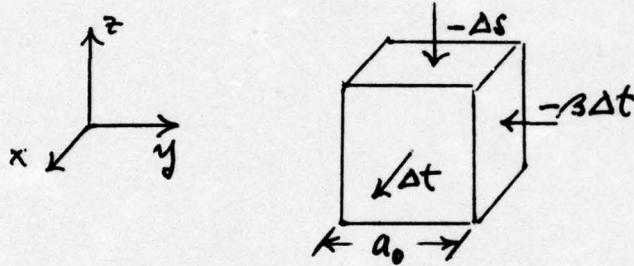


Figure 3. Cubic  $\rightarrow$ orthorhombic "uneven".

$$\bar{\bar{e}} = e \begin{bmatrix} 1 & 0 & 0 \\ 0 & \bar{\alpha} & 0 \\ 0 & 0 & \bar{\alpha} \end{bmatrix} \quad (20)$$

with  $e a_0 = \Delta t$ ,  $\bar{\alpha} e a_0 = \Delta s$ . We may rewrite eq (20) as

$$\bar{\bar{e}} = c_1 e \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} + c_2 e \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 2 \end{bmatrix} + c_3 e \begin{bmatrix} 2 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (21)$$

with  $c_1 = (1-\beta-\alpha)/3$ ,  $c_2 = (\beta-\alpha)/3$ , and  $c_3 = (1+\beta)/3$ . Thus, in the general orthorhombic "uneven" case  $c_1 \neq 0$ , i.e., a  $\Gamma_1$  component is contained in the strain and the star-of- $\bar{k}$  theorem does not hold.

Note: If  $\Delta s = (1-\beta)\Delta t$ , i.e.,  $\alpha = 1-\beta$  so that  $c_1 = 0$ , no  $\Gamma_1$  component is contained (volume is preserved) and the star-of- $\bar{k}$  theorem holds. For this case  $c_2 = (2\beta-1)/3$ ,  $c_3 = (1+\beta)/3$ .

### 3. Cubic $\rightarrow$ trigonal ( $D_{3d}$ ).

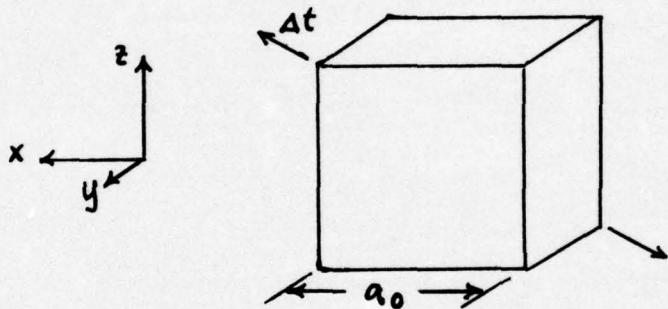


Figure 4. Cubic  $\rightarrow$  trigonal.

$$\bar{e} = e \begin{bmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{bmatrix} \quad (22)$$

with  $2e\sqrt{3} a_0 = \Delta t$ . The operator function is  $yz+xz+xy$ , the sum of the three partners of  $\Gamma_{25}'$ . There is no  $\Gamma_1$  component (volume is preserved); thus, the star-of- $\bar{k}$  theorem holds.

C. Hexagonal Crystals ( $D_{6h}$ )

Axes are defined in Fig. 5. This is consistent with Koster et al.<sup>2</sup>

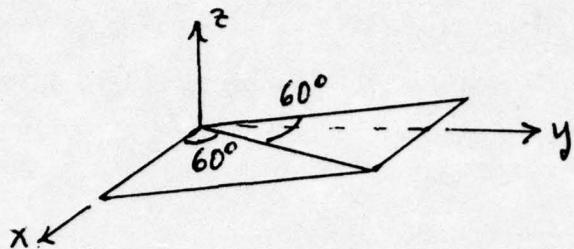


Figure 5. Coordinates for hexagonal crystals.

For hexagonal crystals it is probably most convenient to write an arbitrary strain as

$$\bar{\epsilon} = a \begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{vmatrix} + b \begin{vmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{vmatrix} + c \begin{vmatrix} 1 & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 0 \end{vmatrix} \\ + d \begin{vmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix} + f \begin{vmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{vmatrix} + h \begin{vmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{vmatrix} \quad (23a)$$

<sup>2</sup>"Properties of the Thirty-Two Point Groups", G.F. Koster, J.O. Dimmock, R.G. Wheeler, and H. Statz (M.I.T. Press, 1963).

with  $a = (e_{11} + e_{22})/2$

$b = e_{33}$

$c = (e_{11} - e_{22})/2$

(23b)

$d = e_{12}$

$f = e_{13}$

$h = e_{23}$

The matrices in eq (23a) transform like  $x^2+y^2(\Gamma_1)$ ,  $z^2(\Gamma_1)$ ,  $x^2-y^2(\Gamma_6)$ ,  $xy(\Gamma_6)$ ,  $xz(\Gamma_5)$ , and  $yz(\Gamma_5)$ ; this is consistent with Table C-1 for  $D_{6h}$ . The first two strains in (23a) preserve the hexagonal symmetry; the third strain is associated with an orthorhombic distortion; the last three strains are associated with monoclinic distortions (the  $xy$  distortion forms a monoclinic P lattice, while the  $xz$  and  $yz$  distortions form monoclinic C lattices).

Note: A strain for which  $b = -2a$  in eq (23a) will be volume-preserving (see eq (13)) but will still contain  $\Gamma_1$  so that the star-of-k theorem will not hold.

Examples of specific distortions of hexagonal crystals:

1. Hexagonal  $\rightarrow$  orthorhombic ( $D_{2h}$ ).

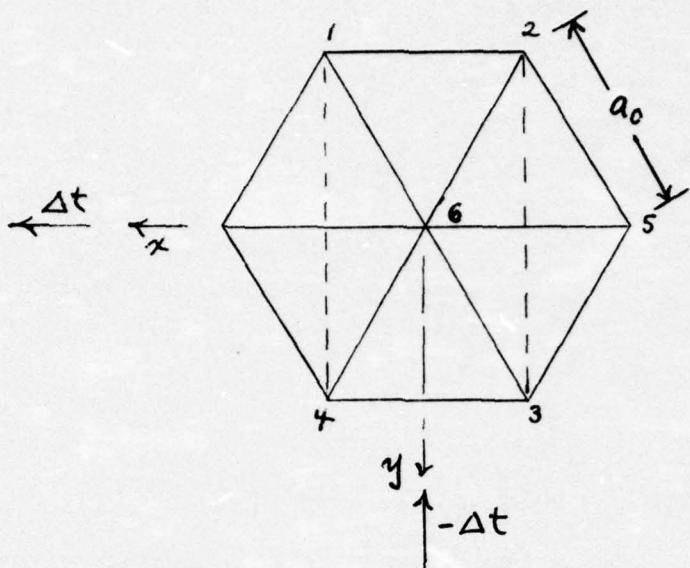


Figure 6. Hexagonal  $\rightarrow$  orthorhombic.

$$\bar{e} = e \begin{bmatrix} 1 & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (24)$$

with  $e a_0 = \Delta t$ . The operator function is  $x^2 - y^2$ , a partner of  $\Gamma_6$ .

Since there is no  $\Gamma_1$  component the star-of- $\bar{k}$  theorem holds. In Fig. 6 the points 1, 2, 3, 4 form the base of the orthorhombic C cell. Before distortion the sides of this cell have the ratio  $\sqrt{3}$  required for a hexagonal crystal; after distortion the ratio becomes

$$\sqrt{3} a_0 (1-e) / a_0 (1+e) = \sqrt{3} (1-2e).$$

2. Hexagonal  $\rightarrow$  monoclinic P ( $C_{2h}$ ).

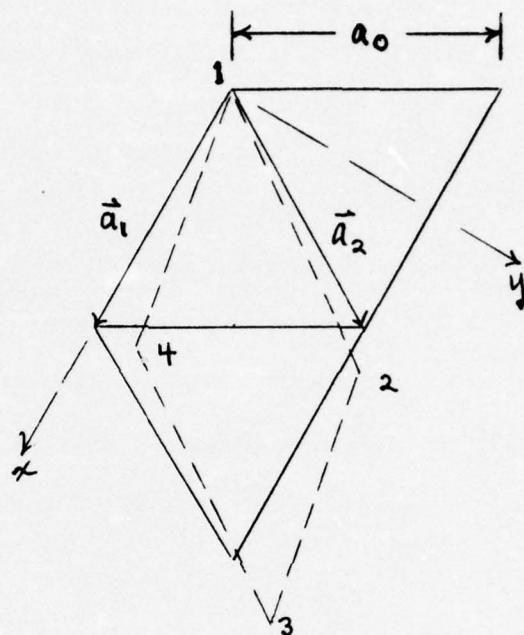


Figure 7. Hexagonal  $\rightarrow$  monoclinic P.

Details of the geometry are given in Appendix F, paragraph 2.

$$\bar{\mathbf{e}} = \mathbf{e} \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (25a)$$

$$a'_1 = a_0, \quad a'_2 = a_0 (1 + \sqrt{3} e/2) \quad (25b)$$

The operator function is  $xy$ , a partner of  $\Gamma_6$ . Since there is no  $\Gamma_1$  component the star-of- $\vec{k}$  theorem holds. In Fig. 7 the dotted lines connecting points 1,2,3,4 form the base of a monoclinic P crystal with angle  $1,4,3 = \beta$ . The vertical sides of the monoclinic P are rectangles with height  $c_0$  (unperturbed hexagonal height).

### 3. Hexagonal $\rightarrow$ monoclinic C ( $C_{2h}$ ) - xz.

In Fig. 6 the points 1,2,3,4 form the base of an orthorhombic C cell. Under xz distortion the vertical (z direction) face with bottom side 1,2 is distorted from a rectangle to a parallelogram and the solid with base 1,2,5,6 and vertical sides forms a primitive cell for the monoclinic C cell (with base 1,2,3,4). Details of the geometry are given in Appendix F, paragraph 3.

$$\bar{e} = e \begin{vmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{vmatrix} \quad (26)$$

The operator function is  $xz$ , a partner of  $\Gamma_5$ . Since no  $\Gamma_1$  component is contained the star-of- $\vec{k}$  theorem holds.

### 4. Hexagonal $\rightarrow$ monoclinic C ( $C_{2h}$ ) - yz.

Again referring to Fig. 6 the points 1,2,3,4 form the base of an orthorhombic C cell. Under yz distortion the vertical (z direction) face with bottom side 2,3 is distorted from a rectangle to a parallelogram. As in the previous case, the solid with base 1,2,5,6 and vertical sides

forms a primitive cell for the monoclinic C cell (with base 1,2,3,4).

Details of the geometry are given in Appendix F, paragraph 4.

$$\bar{e} = e \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix} \quad (27)$$

The operator function is  $yz$ , a partner of  $\Gamma_5$ . Since no  $\Gamma_1$  component is contained the star-of- $\bar{k}$  theorem holds.

Note: the primitive cells for the  $xz$  and  $yz$  distortions do not have the same shape.

#### D. Tetragonal Crystals ( $D_{4h}$ ).

For tetragonal crystals (with z-axis unique) an arbitrary strain can be written as

$$\bar{e} = a \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{bmatrix} + b \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} + c \begin{bmatrix} 1 & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (28a)$$

$$+ d \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} + f \begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix} + h \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix}$$

with  $a = (e_{11} + e_{22})/2$

$$b = e_{33} \quad (28b)$$

$$c = (e_{11} - e_{22})/2$$

$$d = e_{12}$$

$$f = e_{13}$$

(28b)

$$h = e_{23}$$

The first matrix in eq (28a) transforms like  $x^2 + y^2$  ( $\Gamma_1$ ), the second as  $z^2$  ( $\Gamma_1$ ), the third as  $x^2 - y^2$  ( $\Gamma_2$ ), the fourth as  $xy$  ( $\Gamma_3$ ), and the last two as  $xz$  and  $yz$ , respectively (the two partners of  $\Gamma_5$ ); this is consistent with Table C-1 for  $D_{4h}$ .

Note: A strain for which  $b = -2a$  in eq (28a) will be volume-preserving (see eq (13)) but will still contain  $\Gamma_1$  so that the star-of- $\vec{k}$  theorem will not hold.

Examples of specific distortions of tetragonal crystals:

1. Tetragonal  $\rightarrow$  orthorhombic ( $D_{2h}$ ).

(a) "Even".

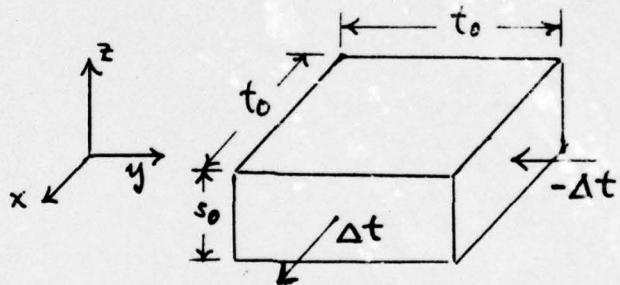


Figure 8. Tetragonal  $\rightarrow$  orthorhombic "even".

$$\bar{e} = e \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (29)$$

with  $et_0 = \Delta t$ . The operator function is  $x^2 - y^2$  ( $\Gamma_2$ ). Since there is no  $\Gamma_1$  component the star-of- $\vec{k}$  theorem holds. Volume is preserved.

(b) "Uneven".

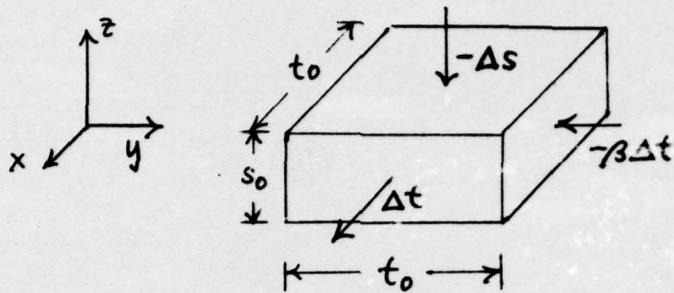


Figure 9. Tetragonal  $\rightarrow$  orthorhombic "uneven".

$$\bar{e} = e \begin{bmatrix} 1 & 0 & 0 \\ 0 & \bar{\alpha} & 0 \\ 0 & 0 & \bar{\alpha} \end{bmatrix} \quad (30)$$

with  $et_0 = \Delta t$ ,  $\alpha e s_0 = \Delta s$ . We may rewrite eq (30) as

$$\bar{e} = c_1 e \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{bmatrix} + c_2 e \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} + c_3 e \begin{bmatrix} 1 & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (31)$$

with  $c_1 = (1 - \beta)/2$ ,  $c_2 = -\alpha$ ,  $c_3 = (1 + \beta)/2$ .

If  $\Delta s = (1 - \beta) (s_0/t_0) \Delta t$ ; i.e.,  $\alpha = (1 - \beta)$ , we see from either (30) or (31) that volume is preserved. However, there are still  $\Gamma_1$  components (unless  $\alpha = 0$  and  $\beta = 1$ ; i.e., the orthorhombic "even" case) so that the star-of- $\vec{k}$  theorem does not hold. The three operator

functions associated with eq (31) are  $x^2+y^2$ ,  $z^2$ , and  $x^2-y^2$ , respectively, or  $c_1 \Gamma_1(1) + c_2 \Gamma_1(2) + c_3 \Gamma_2$ .

2. Tetragonal  $\rightarrow$  orthorhombic C ( $D_{2h}$ ).

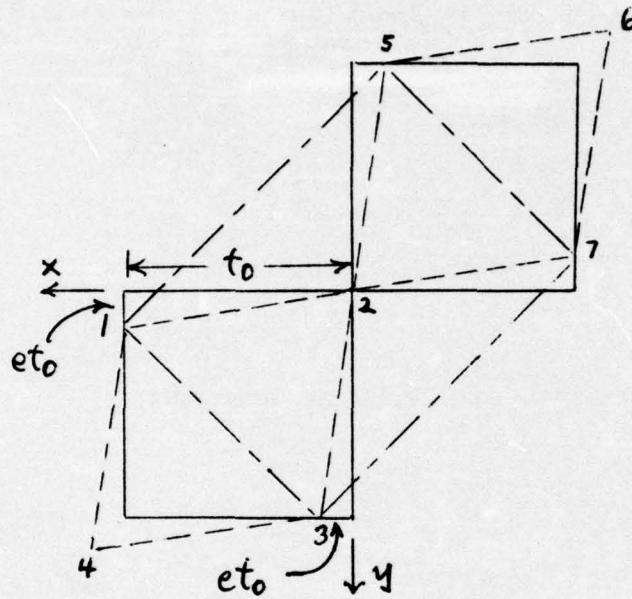


Figure 10. Tetragonal  $\rightarrow$  orthorhombic C.

$$\bar{e} = e \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (32)$$

The operator function is  $xy$  ( $\Gamma_3$ ). Since no  $\Gamma_1$  component is contained the star-of- $\vec{k}$  theorem holds. The solid with base 1,2,3,4 and vertical (z-direction) sides is a primitive cell of the orthorhombic C cell with base 1,5,7,3 and vertical sides. All vertical sides are  $s_0$  (undeformed tetragonal height). The new primitive cell has sides  $t_0$ ,  $t_0$ ,  $s_0$  ( $t_0$

first order); angle 1,2,3 is  $90^\circ - 2e$ . The orthorhombic C cell has base sides 1,3 ( $\sqrt{2}t_0(1-e)$ ) and 3,7 ( $\sqrt{2}t_0(1+e)$ ).

3. Tetragonal  $\rightarrow$  monoclinic P ( $C_{2h}$ ) - xz.

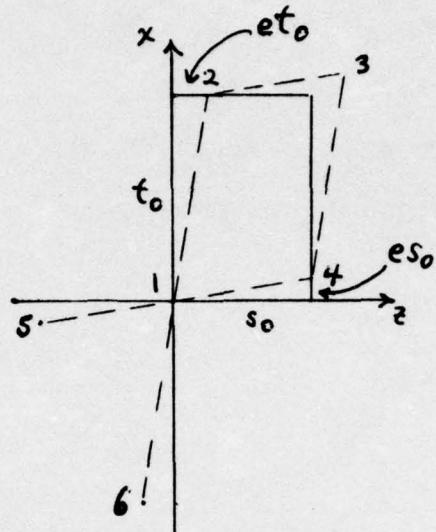


Figure 11. Tetragonal  $\rightarrow$  monoclinic P.

$$\bar{e} = e \begin{vmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{vmatrix} \quad (33)$$

The operator function is xz, a partner of  $\Gamma_5$ . Since no  $\Gamma_1$  component is contained the star-of- $\bar{k}$  theorem holds. After distortion the solid with base 1,2,3,4 and vertical sides (y direction) is a monoclinic P cell with side 1,4 =  $s_0$ , side 1,2 =  $t_0$ , and vertical side  $t_0$ ; angle 2,3,4 is  $90^\circ - 2e$ .

Note 1: The monoclinic P cell used here is "special" in that two sides have the same length  $t_0$ . No new Bravais lattice is thereby created, however, since this cell has no additional symmetry elements

over and above those associated with a cell of identical base but vertical height not equal to  $t_0$ .

Note 2: From Fig. 11 one sees why there is no separately named monoclinic C Bravais lattice with face-center atoms in the non-90°-angle face (base 2,4,6,5); such a lattice can always be considered as monoclinic P with base 1,2,3,4.

Note 3: The tetragonal  $\rightarrow$  monoclinic P ( $C_{2h}$ ) (yz) case is identical to the xz case with the roles of the x and y axes interchanged.

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APPENDIX A  
EQUIVALENT LABELS FOR IRREDUCIBLE REPRESENTATIONS

TABLE A-1. EQUIVALENT LABELS FOR THE CUBIC GROUP ( $O_h$ )

<u>BSW<sup>a</sup></u>	<u>Koster et al.<sup>b</sup></u>	<u>Tinkham<sup>c</sup></u>
$\Gamma_1$	$\Gamma_1^+$	$A_1$
$\Gamma_2$	$\Gamma_2^+$	$A_2$
$\Gamma_{12}$	$\Gamma_3^+$	$E$
$\Gamma_{15}'$	$\Gamma_4^+$	$T_1$
$\Gamma_{25}'$	$\Gamma_5^+$	$T_2$
$\Gamma_1'$	$\Gamma_1^-$	
$\Gamma_2'$	$\Gamma_2^-$	
$\Gamma_{12}'$	$\Gamma_3^-$	
$\Gamma_{15}$	$\Gamma_4^-$	
$\Gamma_{25}$	$\Gamma_5^-$	

<sup>a</sup> Ref 1, Table I. Koster (ref 13, Table XXXI) and Slater (ref 14, Table A3-20) also use the BSW notation.

<sup>b</sup> Ref 2, Table 87. This is also known as the Bethe notation.

<sup>c</sup> Ref 12, Table for O, App B, p. 329. Tinkham gives labels for O (proper rotations only). This is also known as the Mulliken notation.

1. L.P. Bouckaert, R. Smoluchowski, and E. Wigner, Phys. Rev. 50, 58 (1936).
2. "Properties of the Thirty-Two Point Groups," G.F. Koster, J.O. Dimmock, R.G. Wheeler, and H. Statz (M.I.T. Press, 1963).
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14. "Quantum Theory of Molecules and Solids, Vol. 2," J.C. Slater (McGraw-Hill, 1965).

TABLE A-2. EQUIVALENT LABELS FOR THE HEXAGONAL GROUP ( $D_{6h}$ )

<u>Koster et al.<sup>a</sup></u>	<u>Slater<sup>b</sup></u>	<u>Tinkham<sup>c</sup></u>
$\Gamma_1^+$	$\Gamma_1^+$	$A_1$
$\Gamma_2^+$	$\Gamma_2^+$	$A_2$
$\Gamma_3^+$	$\Gamma_4^+$	$B_1$
$\Gamma_4^+$	$\Gamma_3^+$	$B_2$
$\Gamma_5^+$	$\Gamma_6^+$	$E_1$
$\Gamma_6^+$	$\Gamma_5^+$	$E_2$
$\Gamma_1^-$	$\Gamma_1^-$	
$\Gamma_2^-$	$\Gamma_2^-$	
$\Gamma_3^-$	$\Gamma_4^-$	
$\Gamma_4^-$	$\Gamma_3^-$	
$\Gamma_5^-$	$\Gamma_6^-$	
$\Gamma_6^-$	$\Gamma_5^-$	

<sup>a</sup>Ref 2, Table 72. Koster (ref 13, Table XXVI) lists the representations (unlabeled) in the same order.

<sup>b</sup>Ref 14, Table A3-2.

<sup>c</sup>Ref 12, Table for  $D_6$ , App B, p. 327. Tinkham gives labels for  $D_6$  (proper rotations of  $D_{6h}$ ).

2. "Properties of the Thirty-Two Point Groups," G.F. Koster, J.O. Dimmock, R.G. Wheeler, and H. Statz (M.I.T. Press, 1963).
12. "Group Theory and Quantum Mechanics," M. Tinkham (McGraw-Hill, 1964).
13. G.F. Koster, "Space Groups and Their Representations" in "Solid State Physics, Vol. 5," ed. F. Seitz and D. Turnbull (Academic Press, 1957).
14. "Quantum Theory of Molecules and Solids, Vol. 2," J.C. Slater (McGraw-Hill, 1965).

TABLE A-3. EQUIVALENT LABELS FOR THE TETRAGONAL GROUP ( $D_{4h}$ )

<u>This work<sup>a</sup></u>	<u>Koster et al.<sup>b</sup></u>	<u>Koster<sup>c</sup></u>	<u>Slater<sup>d</sup></u>	<u>Tinkham<sup>e</sup></u>
$\Gamma_1$	$\Gamma_1^+$	$M_1$	$\Gamma_1^+$	$A_1$
$\Gamma_2$	$\Gamma_3^+$	$M_3$	$\Gamma_3^+$	$B_1$
$\Gamma_3$	$\Gamma_4^+$	$M_4$	$\Gamma_4^+$	$B_2$
$\Gamma_4$	$\Gamma_2^+$	$M_2$	$\Gamma_2^+$	$A_2$
$\Gamma_5$	$\Gamma_5^+$	$M_5$	$\Gamma_5^-$	$E$
$\Gamma_1'$	$\Gamma_1^-$	$M_1'$	$\Gamma_2^-$	
$\Gamma_2'$	$\Gamma_3^-$	$M_3'$	$\Gamma_4^-$	
$\Gamma_3'$	$\Gamma_4^-$	$M_4'$	$\Gamma_3^-$	
$\Gamma_4'$	$\Gamma_2^-$	$M_2'$	$\Gamma_1^-$	
$\Gamma_5'$	$\Gamma_5^-$	$M_5'$	$\Gamma_5^+$	

<sup>a</sup>  $\Gamma_i$  here is  $X_i(M_i)$  of BSW, ref 1, Table V. This notation is also used in ref 8 and 9.

<sup>b</sup> Ref 2, Table 40.

<sup>c</sup> Ref 13, Table XIV.

<sup>d</sup> Ref 14, Table A3-74.

<sup>e</sup> Ref 12, Table for  $D_4$ , App B, p. 327. Tinkham gives labels for  $D_{4h}$  (proper rotations of  $D_4$ ).

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2. "Properties of the Thirty-Two Point Groups," G.F. Koster, J.O. Dimmock, R.G. Wheeler, and H. Statz (M.I.T. Press, 1963).
8. A.M. Gray, D.M. Gray, and E. Brown, Phys. Rev. B, 11, 1475 (1975).
9. D.M. Gray and A.M. Gray, Phys. Rev. B, 14, 669 (1976).
12. "Group Theory and Quantum Mechanics," M. Tinkham (McGraw-Hill, 1964).
13. G.F. Koster, "Space Groups and Their Representations" in "Solid State Physics, Vol. 5," ed. F. Seitz and D. Turnbull (Academic Press, 1957).
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## APPENDIX B

### PROOF OF COROLLARIES TO THE "STAR-OF- $\vec{k}$ " THEOREM

Corollary 1: For cubic crystals  $\Delta\text{Volume}=0$  is the necessary (N) and sufficient (S) condition for  $\Delta E_F$  (etc.)=0.

N: From the proof<sup>9</sup> of the main theorem, the absence of a  $\Gamma_1$  component in  $\vec{e}$  is the N and S condition that  $\Delta E_F=0$ . The absence of  $\Gamma_1$  implies that the sum of all the operations of the cubic group applied to  $\vec{e}$  equals zero<sup>9</sup>. Since these different rotations must all produce the same volume change,  $\Delta\text{Volume}=0$ . Thus  $\Delta E_F=0 \Rightarrow$  no  $\Gamma_1 \Rightarrow \Delta\text{Volume}=0$ ; then  $\Delta\text{Volume}=0$  is necessary for  $\Delta E_F=0$ . Q.E.D.

S: For a cubic crystal a  $\Gamma_1$  strain (a strain which preserves the cubic symmetry) must always have a volume change associated with it; thus  $\Gamma_1 \Rightarrow \Delta\text{Volume} \neq 0$ . Therefore,  $\Delta\text{Volume}=0 \Rightarrow$  no  $\Gamma_1$ , and, as no  $\Gamma_1 \Rightarrow \Delta E_F=0$ ,  $\Delta\text{Volume}=0$  is sufficient for  $\Delta E_F=0$ . Q.E.D.

Corollary 2: For non-cubic crystals  $\Delta\text{Volume}=0$  is N but not S for  $\Delta E_F$  (etc.)=0.

N: Proof is exactly as in corollary 1.

S: For non-cubic crystals one can preserve the symmetry without changing volume. Consider a tetragonal crystal  $t \times t \times s$ , for example. The distortion  $t \rightarrow t(1+a)$ ,  $s \rightarrow s(1-2a)$  preserves volume to first order. The tetragonal symmetry is preserved; one has merely changed the s/t ratio. Thus  $\Delta\text{Volume}=0$  is not sufficient for  $\Delta E_F=0$ . Q.E.D.

<sup>9</sup>D.M. Gray and A.M. Gray, Phys. Rev. B, 14, 669 (1976).

APPENDIX C

USE OF  $[\Gamma_{xyz}]_s$  TO GENERATE THE REPRESENTATIONS CONTAINED IN  $\bar{e}$

Definition: Given two representations  $\Gamma_m$  and  $\Gamma_n$  of the same group  $\mathcal{H}$  with basis functions  $\phi_1, \dots, \phi_k$  and  $\psi_1, \dots, \psi_\lambda$  respectively, the direct-product matrices  $D(R) = D^m(R) \times D^n(R)$ , with  $R$  any operator in  $\mathcal{H}$ , form a representation of  $\mathcal{H}$  with basis functions  $\phi_i \psi_j$ . If the two sets of functions  $\phi, \psi$  belong to the same representation,  $\Gamma_n$  of  $\mathcal{H}$ , then the "symmetrized-square" representation  $[\Gamma_n]_s$  will be associated with functions of types  $\phi_i \psi_i$  and  $\phi_i \psi_j + \phi_j \psi_i$ ; the "antisymmetrized-square" representation  $[\Gamma_n]_a$  will be associated with functions of type  $\phi_i \psi_j - \phi_j \psi_i$ .

Traces:

$$\text{Direct-product} \quad X^{m \times n}(R) = X^m(R) \times X^n(R)$$

$$\text{Symmetrized-square} \quad 2 X^{(n \times n)s}(R) = [X^n(R)]^2 + X^n(R^2)$$

$$\text{Antisymmetrized-square} \quad 2 X^{(n \times n)a}(R) = [X^n(R)]^2 - X^n(R^2)$$

An arbitrary strain can be represented by six independent  $\bar{e}^{n \times}$  as indicated in eq (14) of the main text, thus six linearly independent functions will be needed; these may be taken as  $x^2, y^2, z^2, xy, xz$ , and  $yz$ . Since basis functions for a direct-product representation are the various products of the basis functions for the original representations, the original  $\Gamma_{xyz}$  with basis functions  $x, y$ , and  $z$  will generate  $xX, xY, xZ, yX, yY, yZ, zX, zY$ , and  $zZ$ . We desire the symmetric functions  $xX (x^2)$ ,  $xY+yX (xy)$ , etc. These six functions will be basis functions for the representation comprising the symmetrized-square of  $\Gamma_{xyz}$ .

( $xY-yX$ , etc. will be associated with the antisymmetrized square.) The 6-dimensional  $[\Gamma_{xyz}]_s$  will be reducible; the contained irreducible representations will be just the irreducible representations required to express the six strain functions and thus just the required set to express an arbitrary strain. (See also ref 12, pp 43-47 and ref 15, pp II-44 to II-48.)

TABLE C-1. IRREDUCIBLE REPRESENTATIONS<sup>a</sup> CONTAINED IN  $[\Gamma_{xyz}]_s$

Point group <sup>a</sup>	$\Gamma_{xyz}$	$[\Gamma_{xyz}]_s$
Cubic ( $O_h$ )	$\Gamma_{15}$	$\Gamma_1 + \Gamma_{12} + \Gamma_{25}'$
Hexagonal ( $D_{6h}$ )	$\Gamma_2^- + \Gamma_5^-$	$2\Gamma_1 + \Gamma_5 + \Gamma_6$
Tetragonal ( $D_{4h}$ )	$\Gamma_4' + \Gamma_5'$	$2\Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_5$
$O$	$\Gamma_4$	$\Gamma_1 + \Gamma_3 + \Gamma_5$
$T_d$	$\Gamma_5$	$\Gamma_1 + \Gamma_3 + \Gamma_5$
$T_h$	$\Gamma_4^-$	$\Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_4$
$T$	$\Gamma_4$	$\Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_4$

<sup>12</sup>"Group Theory and Quantum Mechanics," M. Tinkham (McGraw-Hill, 1964).

<sup>15</sup>Lecture notes on "Theory of the Properties of Ionic Complexes in Crystals," Frank Ham, RPI, 1969 (unpublished).

TABLE C-1. IRREDUCIBLE REPRESENTATIONS<sup>a</sup> CONTAINED IN  $[\Gamma_{xyz}]_s$ 

$C_{4h}$	$\Gamma_1^- + \Gamma_3^- + \Gamma_4^-$	$2\Gamma_1 + 2\Gamma_2 + \Gamma_3 + \Gamma_4$
$D_4$	$\Gamma_2 + \Gamma_5$	$2\Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5$
$C_{4v}$	$\Gamma_1 + \Gamma_5$	$2\Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5$
$D_{2d}$	$\Gamma_4 + \Gamma_5$	$2\Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5$
$D_6$	$\Gamma_2 + \Gamma_5$	$2\Gamma_1 + \Gamma_5 + \Gamma_6$
$C_{6v}$	$\Gamma_1 + \Gamma_5$	$2\Gamma_1 + \Gamma_5 + \Gamma_6$
$D_{3h}$	$\Gamma_4 + \Gamma_6$	$2\Gamma_1 + \Gamma_5 + \Gamma_6$
$C_{6h}$	$\Gamma_1^- + \Gamma_5^- + \Gamma_6^-$	$2\Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_5 + \Gamma_6$
$D_{3d}$	$\Gamma_2^- + \Gamma_3^-$	$2\Gamma_1 + 2\Gamma_3$
$D_{2h}$	$\Gamma_2^- + \Gamma_3^- + \Gamma_4^-$	$3\Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_4$
$D_2$	$\Gamma_2 + \Gamma_3 + \Gamma_4$	$3\Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_4$
$C_{2v}$	$\Gamma_1 + \Gamma_2 + \Gamma_4$	$3\Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_4$
$C_{2h}$	$\Gamma_1^- + 2\Gamma_2^-$	$4\Gamma_1 + 2\Gamma_2$
$C_6$	$\Gamma_1 + \Gamma_5 + \Gamma_6$	$2\Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_5 + \Gamma_6$
$C_{3h}$	$\Gamma_2 + \Gamma_3 + \Gamma_4$	$2\Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_5 + \Gamma_6$
$D_3$	$\Gamma_2 + \Gamma_3$	$2\Gamma_1 + 2\Gamma_3$

TABLE C-1. IRREDUCIBLE REPRESENTATIONS<sup>a</sup> CONTAINED IN  $[\Gamma_{xyz}]_s$

$C_{3v}$	$\Gamma_1 + \Gamma_3$	$2 \Gamma_1 + 2 \Gamma_3$
$C_{3i}$	$\Gamma_1^- + \Gamma_2^- + \Gamma_3^-$	$2 \Gamma_1 + 2 \Gamma_2 + 2 \Gamma_3$
$C_4$	$\Gamma_1 + \Gamma_3 + \Gamma_4$	$2 \Gamma_1 + 2 \Gamma_2 + \Gamma_3 + \Gamma_4$
$S_4$	$\Gamma_2 + \Gamma_3 + \Gamma_4$	$2 \Gamma_1 + 2 \Gamma_2 + \Gamma_3 + \Gamma_4$
$C_3$	$\Gamma_1 + \Gamma_2 + \Gamma_3$	$2 \Gamma_1 + 2 \Gamma_2 + 2 \Gamma_3$
$C_2$	$\Gamma_1 + 2 \Gamma_2$	$4 \Gamma_1 + 2 \Gamma_2$
$C_s$	$2 \Gamma_1 + \Gamma_2$	$4 \Gamma_1 + 2 \Gamma_2$
$C_i$	$3 \Gamma_1^-$	$6 \Gamma_1$
$C_1$	$3 \Gamma_1$	$6 \Gamma_1$

<sup>a</sup>Notation is as indicated in the section thereon in the main text.

APPENDIX D  
SUBGROUP DECOMPOSITION OF THE 32 POINT GROUPS

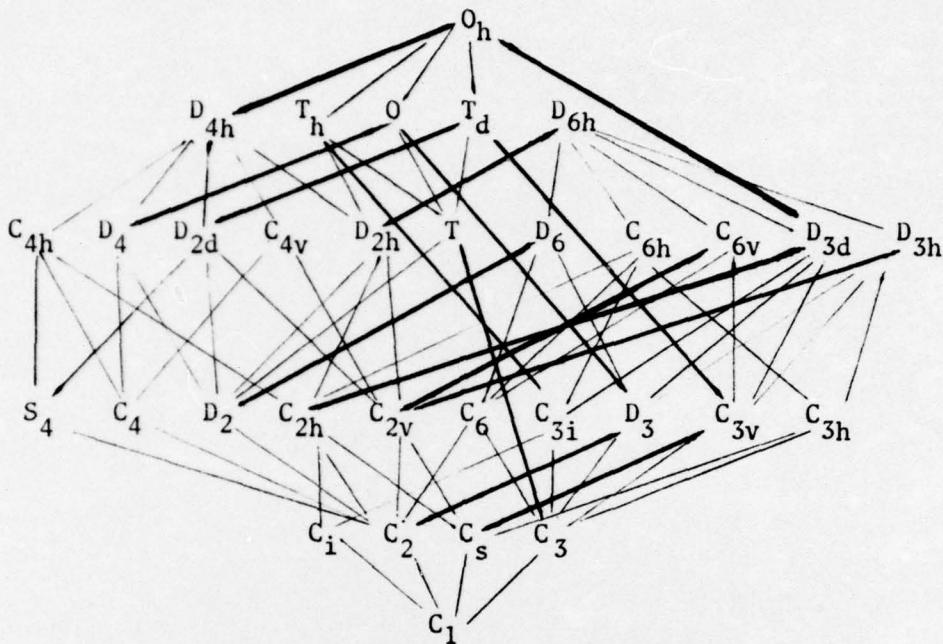


Figure 12. Subgroup decomposition of the 32 point groups. A heavy line indicates that the subgroup is not invariant.

In Fig. 12, all of the 32 point groups are illustrated along with the possible subgroups of each of these groups. Light lines indicate invariant subgroups, heavy lines indicate non-invariant subgroups. (Fig. 12 is taken directly from ref 2; compatibility tables connecting these groups are given therein.)

<sup>2</sup>"Properties of the Thirty-Two Point Groups", G.F. Koster, J.O. Dimmock, R.G. Wheeler, and H. Statz (M.I.T. Press, 1963).

## APPENDIX E

### TRANSFORMATION PROPERTIES OF OPERATORS DETERMINED BY TRANSFORMATION PROPERTIES OF BASIS FUNCTIONS

When the desired strain  $\bar{e}$  decomposes into  $\sum_{i,\alpha} c_{i\alpha} \bar{e}^{i\alpha}$  it is not always apparent how the various  $\bar{e}^{i\alpha}$  transform. If one knows how basis functions for various representations transform it may be easier to first associate functions  $f_{i\alpha}^i(\vec{r})$  with the various  $\bar{e}^{i\alpha}$ . We now show that for

$$f_{i\alpha}^i(\vec{r}) \equiv \vec{r}_T \bar{e}^{i\alpha} \vec{r}, \quad (E-1)$$

then the  $\bar{e}^{i\alpha}$  transform like the  $f_{i\alpha}^i(\vec{r})$ . Here  $\vec{r}$  is the column vector

$$\vec{r} \equiv \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

and  $\vec{r}_T$  is the row vector

$$\vec{r}_T \equiv (x, y, z).$$

Proof: The necessary and sufficient condition that a matrix  $\bar{e}^{i\alpha}$  transform like representation  $i$  is that

$$P_R(\bar{e}^{i\alpha}) P_R^{-1} = \sum_{\lambda} D_{\lambda\alpha}^i(R) \bar{e}^{i\lambda} \quad (E-2)$$

for all operators  $R$  of the pertinent group. Multiply eq (E-2) by  $\vec{r}_T$  from the left and by  $\vec{r}$  from the right:

$$\vec{r}'_T \bar{e}^{i\alpha} \vec{r}' = \sum_{\lambda} D_{\lambda\alpha}^i(R) f_{i\lambda}^i(\vec{r}), \quad (E-3)$$

using (E-1) and  $P_R^{-1} \vec{r} = \vec{r}'$ . From the definition of  $f_{i\lambda}^i(\vec{r})$  in (E-1), the left side of (E-3) is just  $f_{i\alpha}^i(\vec{r}')$ ; thus (E-3) becomes

$$f_{i\alpha}^i(\vec{r}') = f_{i\alpha}^i(R^{-1} \vec{r}) = \sum_{\lambda} D_{\lambda\alpha}^i(R) f_{i\lambda}^i(\vec{r}).$$

If this is repeated for  $\alpha = 1, 2, \dots, d$  where  $d$  is the dimensionality of

representation  $i$ , then

$$\begin{pmatrix} f_1^i(R^{-1}\hat{r}) \\ \vdots \\ f_d^i(R^{-1}\hat{r}) \end{pmatrix} = \begin{bmatrix} \tilde{D}^i(R) \end{bmatrix} \begin{pmatrix} f_1^i(\hat{r}) \\ \vdots \\ f_d^i(\hat{r}) \end{pmatrix} \quad (E-4)$$

Since eq (E-4) is true for all  $R$ , this is just the condition that the  $f_\alpha^i(\hat{r})$  transform like representation  $i$ , i.e., that the  $f_\alpha^i(\hat{r})$  defined by eq (E-1) are basis functions for representation  $i$ . Thus, the transformation properties of the  $\tilde{e}^{i\alpha}$  are the same as those of the  $f_\alpha^i$  defined by eq (E-1), Q.E.D.

APPENDIX F  
HEXAGONAL CASE: GEOMETRIC DETAILS

1.  $\Gamma_1$  strains.

(a) For a strain associated with  $x^2+y^2$  ( $e_{11} = e_{22} = e$ , all other  $e_{ij} = 0$ ) every vector in the xy plane will simply be extended by a factor  $(1+e)$ . Thus, the hexagonal symmetry is maintained; one merely decreases the c/a ratio (for positive e).

(b) For a strain associated with  $z^2$  ( $e_{33} = e$ , all other  $e_{ij} = 0$ ) the hexagonal symmetry is clearly maintained; one merely increases the c/a ratio (for positive e).

2. The  $\Gamma_6$  strain xy.

For a strain associated with  $xy$ ,  $e_{12} = e_{21} = e$ , all other  $e_{ij} = 0$ . Referring to Fig. 7 in the main text

$$\vec{a}_{10} = a\hat{i}, \quad \vec{a}_{20} = (a/2)\hat{i} + (\sqrt{3}a/2)\hat{j}.$$

Using eq (12) of the main text these become

$$\begin{aligned}\vec{a}_1 &= a\hat{i} + ea\hat{j} \\ \vec{a}_2 &= a(1/2 + \sqrt{3}e/2)\hat{i} + a(\sqrt{3}/2 + e/2)\hat{j}.\end{aligned}$$

To first order  $a_1 = a$ ,  $a_2 = a(1 + \sqrt{3}e/2)$ , and the angle between  $\vec{a}_1$  and  $\vec{a}_2$  is  $60^\circ - 3e/2$ . The detailed geometry of this distortion is indicated in Fig. 13.

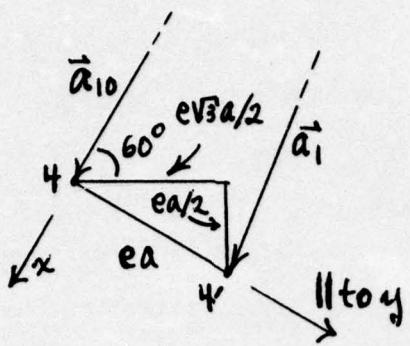


Figure 13a. Geometry at point 4 of Figure 7.

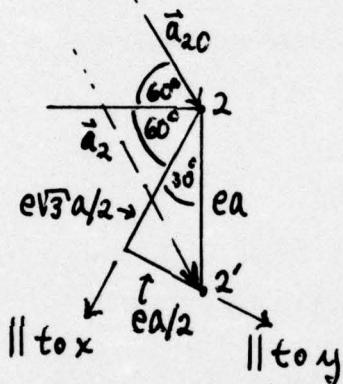


Figure 13b. Geometry at point 2 of Figure 7.

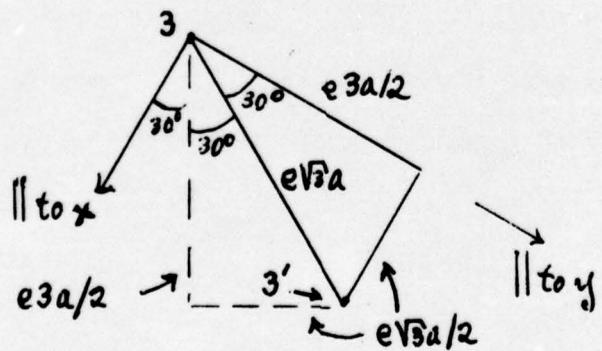


Figure 13c. Geometry at point 3 of Figure 7.

### 3. The $\Gamma_5$ strain $xz$ .

In Fig. 6 of the main text take the origin at point 2, x-axis toward point 1, y-axis toward point 3, and z-axis vertically up from the plane of the figure. Before distortion the points 1,2,3,4 form the base of an orthorhombic C solid. Under xz distortion a non-90° angle is produced in the vertical side with bottom edge 2,1. Define  $\vec{a}_{10}$  as the undistorted vector from the origin to point 1,  $\vec{a}_{30}$  as the vector from the origin to point 3, and  $\vec{c}_0$  as the pertinent vertical vector.

### Under xz distortion

$$\vec{a}_1 = a_0 \hat{i} + e a_0 \hat{k}$$

$$\vec{a}_3 = \vec{a}_{30} = \sqrt{3}a_0 \hat{j}$$

$$\vec{c} = ec_o \hat{i} + c_o \hat{k}$$

so that, to first order,  $a_1 = a_0$ ,  $a_3 = \sqrt{3}a_0$ ,  $c = c_0$ , and the angle  $\beta$  between  $\vec{a}_1$  and  $\vec{c}$  is  $90^\circ - 2e$ . A perspective drawing is shown in Fig. 14. In this figure, the

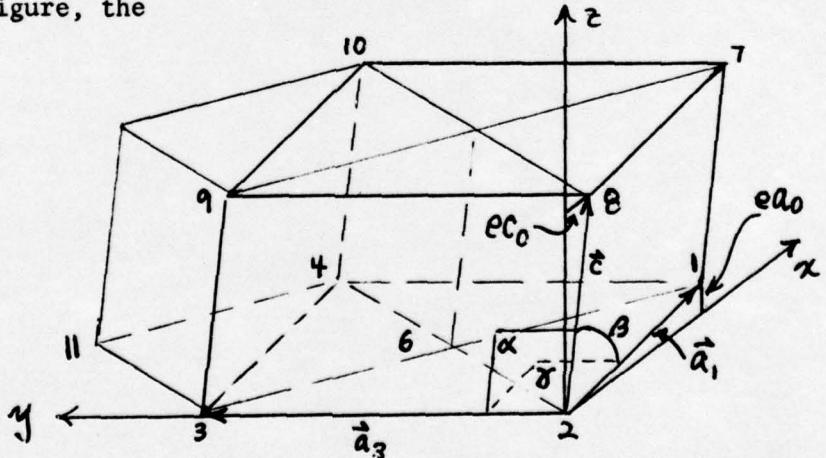


Figure 14. Perspective drawing for the hexagonal  $\Gamma_5$  strain  $xz$ .

monoclinic C cell is outlined by points 1-4, 7-10;  $\alpha = \gamma = 90^\circ$ ,  $\beta = 90^\circ - 2e$ .

The primitive cell is outlined by points 4,6,3,11, etc, side 4,6 =  $a_0$ , side 6,3 =  $a_0$ , side 3,9 =  $c_0$ , angle 6,3,11 =  $120^\circ$ , angle 6,3,9 =  $90^\circ - e$ .

#### 4. The $\Gamma_5$ strain $yz$ .

In Figure 6 of the main text take the origin at point 2, x-axis toward point 1, y-axis toward point 3, and z-axis vertically up from the plane of the figure (exactly as in the  $xz$  case). Before distortion the points 1,2,3,4 form the base of an orthorhombic C solid. Under  $yz$  distortion a non- $90^\circ$  angle is produced in the vertical side with bottom edge 2,3. Define  $\vec{a}_{10}$ ,  $\vec{a}_{30}$ , and  $\vec{c}_0$  as in the previous section. Under  $yz$  distortion

$$\vec{a}_1 = \vec{a}_{10} = a_0 \hat{i}$$

$$\vec{a}_3 = \sqrt{3}a_0 \hat{j} + \sqrt{3}ea_0 \hat{k}$$

$$\vec{c} = ec_0 \hat{j} + c_0 \hat{k}$$

so that, to first order,  $a_1 = a_0$ ,  $a_3 = \sqrt{3}a_0$ ,  $c = c_0$ , and the angle  $\beta$  between  $\vec{a}_3$  and  $\vec{c}$  is  $90^\circ - 2e$ . A perspective drawing is shown in Fig. 15.

In this figure, the

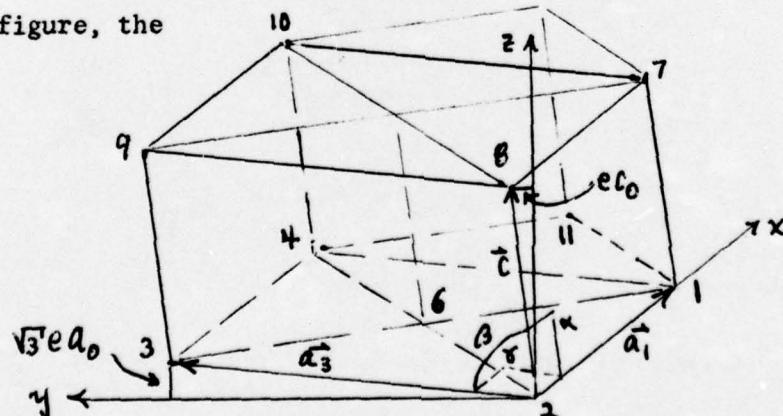


Figure 15. Perspective drawing for the  $\Gamma_5$  strain  $yz$ .

monoclinic C cell is outlined by points 1-4, 7-10;  $\alpha = \gamma = 90^\circ$ ,  
 $\beta = 90^\circ - 2e$ . The primitive cell is outlined by points 4,6,1,11 etc;  
side 1,6 =  $a_0$ , side 1,11 =  $a_0$ , side 1,7 =  $c_0$ , angle 4,6,1 =  $120^\circ$ ,  
angle 6,1,7 =  $90^\circ - \sqrt{3}e$ .

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